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SYNTHESIS AND CHARACTERIZATION OF DICHLORO O, O'-ETHYLENE-N, N'-ETHYLENEBIS - (SALICYLIDENEIMINATO)COPPER(II)

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الملخص

العنوان هو مركب يحتوي على مواقع مانحة من النيتروجين والاكسجين (N_2O_2) وحضر عن طريق تفاعل ايثيلين ساليسيلات الامين مع هيدروكسيد الصوديوم وثنائي برومو الايثان في مزيج من الميثانول : الماء (٤٠:٦٠) بنسبة ١:٢:١، على التوالي، متبوع باضافة كلوريد النحاس (١ مول) . صنف هذا المركب بناءا على اسس التحليل العنصري ومعطيات التحليل الطيفي (الاشعة تحت الحمراء، الاشعة الفوق بنفسجية ورنين متوازي المغنطسية الالكتروني)، ودراسة الكيمياء الكهربائية، والقابلية المغنطسية، وقياس الموصلية الكهربائية. تبين نتائج هذه الدراسات أن هذا المركب ذو الحلقة الكبيرة يتميز بأنه غير ايوني وأن ايون النحاس متوازي المغنطسية ويحافظ على شكله ثماني الاسطح لأنه محاط بستة ذرات $N_2O_2Cl_2$. تشير دراسة التحليل الفلطي الدوري على ان ايون النحاس ذو الشحنة الثنائية الموجبة هو الايون الظاهر في هذا المركب.

ABSTRACT

The title complex, containing N_2O_2 donor sites, synthesized by reacting N, N′-ethylene bis (salicylideneiminate) with sodium hydroxide and dibromoethane in a methanol: water (60:40) mixture in a 1:2:1 ratio, respectively, followed by the addition of cupric chloride (1 mol) has been characterized by elemental analysis, spectroscopic data (IR, electronic and EPR), electrochemical study, magnetic susceptibility and conductivity measurements. The results of these studies reveal that the macrocyclic complex is non-ionic and copper(II) is paramagnetic and maintains its octahedral configuration by being surrounded by six atoms (two Cl, two O and two N). Cyclic voltammetric study indicates that Cu(II) is the prominant form in this complex.

INTRODUCTION

There has been keen interest in the synthesis of macrocylic complexes containing oxa-aza moiety. This is due to the fact that they are structurally similar to the polyoxa macrocyclic complexes. However, the presence of the donor atoms, in the former, has been proved to result in more stable complexes with a metal ion.[1] Investigations of the oxa-aza macrocyclic ligands with metal ions indicate that such ligands exhibit a larger stability constant[2,3] than does the oxa analogue[4]. Macrocyclic ligands containing oxa-aza groups would be expected to form more stable complexes[5,6], by virtue of the presence of the amine donor, than the oxa analogues[4,7] . Therefore, it seemed appropriate and important to study the behaviour of a novel oxa-aza macrocyclic ligand towards a transition metal ion. This paper reports, in particular, the synthesis of a template dioxa-diaza macrocyclic complex of copper(II), dichloro O, O′-ethylene-N, N′-ethylene bis (salicylideneiminato) copper(II).

EXPERIMENýTAL

Ethylenediamine, salicylaldehyde, sodium hydroxide, dibromo-ethane and hydrated cupric chloride (BDH) were used as received. All solvents were distilled and dried before use. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Perkin- Elmer 240°c microanalyser. Chlorine was estimated by the usual gravimetric method as AgCl. Metal analysis was made on a Schimadzu AA-6A0 Atomic Absorption/Flame Emission spectrophotometer. Solid state I.R. spectrum (as KBr disc) was measured on a Pye-Unicam SP3-300 IR spectrophotometer. X-band EPR spectrum was recorded on a Bruker ER 200D spectrometer equipped with a variable temperature device. Magnetic susceptibility of the complex was measured using a Cahn 2000 Faraday magnetic balance calibrated with $Hg[Co(NCS)_4]$ at room temperature. Conductivity was measured in acetonitrile at room temperature using a Metrohm 660 conductometer. Diffuse reflectance spectrum was recorder on a Hitachi 300 UV-vis spectrophotometer, fitted with a standard reflectance attachment. Cyclic voltammogram was recorded using an EG & G (PAR) equipped with model 174XY recording system with a working platinum electrode and a counter platinum electrode vs a saturated calomel electrode (SCE) using tetrabutylammonium perchlorate (0.01 M) as a supporting electrolyte in acetonitrile.

Synthesis of N, N′-ethylenebis(salicylideneiminate)

It was synthesized as described previously[8] .

Synthesis of dichloro O, O′-ethyleneN, N′-ethylenebis(salicylidene -iminato)copper(II)

A dropwise addition of sodium hydroxide (0.8 g, 0.02 mol) dissolved in a minimum quantity of water was made to a methanol: water mixture (60:40) (100 cm^3) of the Schiff base, N,N′-ethylene-bis -(salicylideneiminate) (2.94 g, 0.01 mol). This solution colour changed from yellow to deep red after being stirred under reflux for 6 hours. Dibromoethane (1.88 g, 0.01 mol) was added slowly to the hot solution, and stirring was continued for another 6 hours. This mixture was reduced to half the volume on a heated water bath. The addition of cupric chloride (1.70 g, 0.01 mol), dissolved in methanol (20 cm^3), to the concentrated solution, afforded immediately a microcrystalline dark green product which was stirred for half an hour and cooled at room temperature. The precipitate thus obtained was filtered, washed with water and methanol and dried in vacuo. M.P., 280°C (decomp); % yield, 65. Found: C, 50.5; H, 4.0; N, 6.4; Cl, 16.4; Cu, 14.5 Calc: C, 50.4; H, 4.2; N, 6.5; Cl, 16.5; Cu, 14.8 .

RESULT AND DISCUSSION

The reaction of N, N′-ethylene-bis(salicylideneiminate) and sodium hydroxide with dibromoethane followed by the addition of hydrated curic chloride in a mixture of methanol: water (60:40) in a 1:2:1:1 ratio, respectively, yields the macrocyclic complex, dichloro O, O′-ethylene-N, N′-ethylenebis(salicylideneiminato)copper(II) as a microcrystalline compound. It is stable in the solid state and decomposes quickly in concentrated nitric acid. It is soluble in acetonitrille, nitromethane, THF, DMSO and very dilute HNO_3 solution. The relativity low value of molar conductance of 10^{-3} M solution of the complex measured in acetonitrile (40 Ω^{1-} mol^{-1} cm^2) and the insolubility of this complex in water reveal its predominantly non-ionic nature[9]. Furthermore, the complex does not show high tendency to dissociate. The elemental analyses recorded for the complex conform to the proposed composition (Scheme 1).

The IR spectral data of the complex are conclusive (Fig. 1). No peak near 3500 cm^{-1} assignable to O-H stretching frequency was observed, indicating that the cyclisation reaction took place. It is known that the C-O stretching mode for alcohols, ethers, carboxylic acids and esters appears in the 1050-1300 cm^{-1} range[10]. In the IR spectrum of the complex, the υ(C-O) is observed at 1230 cm^{-1}, and this agrees well with the reported compounds. Three distinct bands seen at 1530 cm^{-1},

1380 cm^{-1} and 1060 cm^{-1} have been assigned to υ(C=N), υ(C-N) and υ(C-C), respectively. Two strong absorption bands have also been observed at 3061 cm^{-1} and 370 cm^{-1} attributable certainly to copper-nitrogen and copper-oxygen stretching modes, respectively. The υ(Cu-Cl) appeared as a sharp absorption band at 470 cm^{-1}. However, the C-H stretching frequency appeared at its proper position (2980 cm^{-1}).

The room temperature microcrystaline powder EPR spectrum shows an axial signal with g_{11} = 2.268 and $g_{\perp}$ =2.056 (g_0 = 2.13), in agreement with the elongated rhombic octahedral stereochemistry of the copper(II) ion[10]. The nuclear hyperfine coupling is observed in the g_{11} signal with three of the four components resolved, the last one being obscured by the $g_{\perp}$ component. Lowering the temperature to 110 K narrows the signal but the g values remain unaltered. Therefore, the orbital ground state of the copper(II) would be basically $d_{x^2-y^2}$ and the $CuN_2O_2Cl_2$ would be statistically distorted.

The diffuse reflectance spectrum of the complex recorded in acetonitrile shows a broad band centered at 820 nm which is characteristic of the d-d transition (x^2-y^2 $\rightarrow z^2$) in the d^9 system of the copper(II) ion. The observed magnetic moment value of the complex (1.70 μB) also supports the d^9 configuration, i.e, the presence of one unpaired electron in the copper(II) ion. On the other hand, the cyclic voltammogram of the complex redorded in acetonitrile exhibits one cathodic and one anodic waves corresponding to a reversible one step redox process Cu^{II}/Cu^{I}. This implies that Cu^{II} is the stable form in the macrocyclic complex.

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